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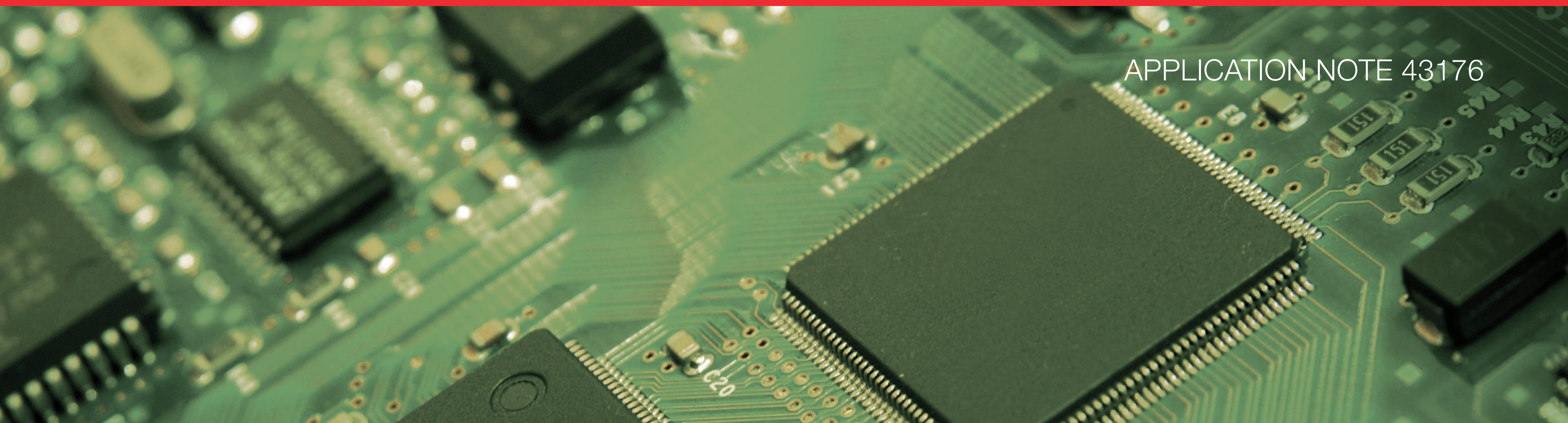

APPLICATION NOTE 43176

Routine determination of ultratrace elements in semiconductor grade nitric acid by the Thermo Scientific iCAP RQ ICP-MS

Authors

Tomoko Vincent[1], Jones Hsu[2], Vicki Wu[3], Julian Wills[1]

[1]Thermo Fisher Scientific, Bremen, Germany

[2]BASF, Taipei, Taiwan

[3]Joy Allied Technology, Taipei, Taiwan

Keywords

Cold plasma, high sensitivity, iCAP RQ, QCell, semiconductor

Goal

To determine ultratrace metal concentrations in semiconductor grade nitric acid (HNO_3). Demonstrate the use of cold plasma (CP) and kinetic energy discrimination (KED) to reduce background equivalent concentrations (BEC) and improve detection limits (LoD). Demonstrate the use of the Thermo Scientific™ iCAP™ RQ ICP-MS to perform reproducible ultratrace ng·L^{-1} (ppt) measurements of semiconductor relevant elements in nitric acid.

Introduction

The Thermo Scientific™ iCAP™ RQ ICP-MS has been specifically developed for ultratrace elemental analysis in applications such as semiconductor, nuclear and geoscience that require the highest elemental sensitivity. The iCAP RQ ICP-MS is equipped with an inert sample introduction system and a high transmission interface. Through the combination of a lightning fast, solid state, dynamic frequency RF generator, proprietary 90 degree ion optics and effective interference removal using the Thermo Scientific QCell™ collision/reaction cell (CRC), the iCAP RQ ICP-MS provides the high elemental sensitivity and low backgrounds required for ultratrace elemental analyses.

In semiconductor manufacturing support applications (for example, incoming supplier or process control) target concentrations are generally below 10 ng·L^{-1}. In this note, a single ICP-MS measurement using three instrumental modes (hot plasma, cold plasma and hot plasma with KED) was used for the analysis of semiconductor grade nitric acid.

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For many elements, the use of single mode He KED with hot plasma (HP) is sufficient for the suppression of background and sample matrix induced spectral interferences to allow for reliable measurement at these concentration levels. For some elements however, in particular first and second group metals as well as some transition metals, analysis using cold plasma is preferable to hot plasma since contamination from the sample introduction system is reduced, leading to lower backgrounds and improved detection power.

Sample and calibration solution preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ) and left to dry in a laminar flow clean hood before use. Multielement standards at concentrations of 50, 100, 500 and 1000 ng·L^{-1} were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (SPEX Certiprep, Metuchen, USA) directly to the 1% HNO_3 samples. In order to assess recovery in the 1% HNO_3, a spike recovery test at 10 ng·L^{-1} was performed. Semiconductor grade HNO_3 (Fisher Scientific OPTIMA™) was used for the rinse and blank solutions.

Instrument configuration

The iCAP RQ ICP-MS was configured for routine ultratrace elemental analyses in semiconductor applications. The instrument configuration and operation parameters are shown in Table 1. The iCAP RQ ICP-MS used in this study was not installed in a cleanroom.

The iCAP RQ ICP-MS was equipped with a self-aspirating PFA 100 MicroFlow nebulizer (ESI, Omaha, USA), a peltier cooled quartz spraychamber (operating at 3 °C), a 2.0 mm ID sapphire injector and a demountable quartz torch.

Table 1. Instrument configuration.

Parameter	Value
Spraychamber	Quartz, cyclonic
Nebulizer	MicroFlow PFA-100 (self- aspirating)
Injector	2.0mm I.D., sapphire
Interface	Platinum sampler and high sensitivity platinum skimmer
Extraction Lens System	Cold plasma

	Hot plasma	Cold plasma	KED
Forward Power	1550 W	550 W	1550 W
Auxiliary	0.8 L·min^{-1}		
Cool Gas	14 L·min^{-1}		
Nebulizer Gas	0.9 L·min^{-1}	0.74 L·min^{-1}	0.9 L·min^{-1}
CRC Gas	-	-	pure He gas at 3.5 mL·min^{-1}
KED	-	-	2 V
Dwell Time	100 to 300 ms per peak, 3 sweeps		

Results

Background equivalent concentrations (BEC) and detection limits (LoD), based on three times the standard deviation of ten replicate measurements of the calibration blank, were determined for 64 elements in 1% HNO_3. Each sample was analyzed in a single mixed mode acquisition with automated switching between hot and cold plasma using the same instrument configuration. Results from this measurement as well as percentage recoveries from a 10 ng·L^{-1} spike recovery test are presented in Table 2.

Table 2. Detection limit (LoD) and background equivalent concentration (BEC) and 10 ng·L^{-1} recovery data for 1% HNO_3 using the iCAP RQ ICP-MS. Please note that BEC and LoD values are dependent on the sample measured and were obtained in a non-cleanroom environment. Recovery values are shown as the percentage recovery for a 10 ng·L^{-1} spike in 1% HNO_3.

Analyte	Mode	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{7}Li	Cold	0.03	0.04	96
^{9}Be	Hot	0.5	0.3	101
^{11}B	Hot	2.0	11	107
^{23}Na	Cold	0.2	0.2	114
^{24}Mg	Cold	0.02	0.06	101
^{27}Al	Cold	0.3	0.8	108
^{39}K	Cold	0.7	5.2	108
^{40}Ca	Cold	2.5	5.1	106
^{45}Sc	KED	0.7	0.6	104
^{48}Ti	KED	0.8	0.3	94
^{51}V	KED	0.5	0.2	98
^{52}Cr	Cold	0.3	0.3	98
^{55}Mn	Cold	0.1	0.06	98
^{56}Fe	Cold	0.6	1.9	95
^{58}Ni	Cold	0.3	0.5	103
^{59}Co	Cold	0.09	0.03	99
^{63}Cu	Cold	0.5	0.5	96
^{66}Zn	Cold	0.01	0.01	101
^{71}Ga	Hot	0.13	0.14	103
^{74}Ge	KED	0.8	0.09	100
^{75}As	KED	0.9	0.3	94
^{78}Se	KED	0.01	0.01	112
^{85}Rb	Cold	0.8	1.4	100
^{89}Y	Hot	0.02	0.01	100
^{90}Zr	Hot	0.09	0.06	92
^{93}Nb	Hot	0.02	0.01	96
^{98}Mo	Hot	0.5	1.2	99
^{101}Ru	Hot	0.08	0.02	99
^{103}Rh	Hot	0.04	0.01	101
^{105}Pd	Hot	0.13	0.07	99
^{107}Ag	Hot	0.25	0.64	96
^{111}Cd	Hot	0.32	0.13	99
^{115}In	Hot	0.08	0.11	100
^{118}Sn	Hot	0.83	2.39	103
^{121}Sb	Hot	0.12	0.05	104
^{125}Te	Hot	0.46	0.1	100
^{133}Cs	Hot	0.21	1.77	99
^{137}Ba	Hot	0.36	0.13	98
^{139}La	Hot	0.01	0.001	99
^{140}Ce	Hot	0.01	0.002	102
^{141}Pr	Hot	0.003	0.001	99
^{146}Nd	Hot	0.05	0.01	101
^{147}Sm	Hot	0.04	0.01	100

Analyte	Mode	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{153}Eu	Hot	0.01	0.003	99
^{157}Gd	Hot	0.03	0.006	101
^{159}Tb	Hot	0.001	0.001	99
^{163}Dy	Hot	0.02	0.002	100
^{165}Ho	Hot	0.001	0.001	99
^{166}Er	Hot	0.01	0.003	103
^{169}Tm	Hot	0.003	0.001	100
^{172}Yb	Hot	0.01	0.001	100
^{175}Lu	Hot	0.01	0.001	99
^{178}Hf	Hot	0.03	0.01	101
^{181}Ta	Hot	0.01	0.001	94
^{182}W	Hot	0.33	0.65	102
^{185}Re	Hot	0.03	0.01	96
^{193}Ir	Hot	0.01	0.002	96
^{195}Pt	Hot	0.25	0.6	100
^{197}Au	Hot	0.10	0.08	103
^{202}Hg	Hot	0.48	1.4	104
^{205}Tl	Hot	0.09	0.17	98
^{208}Pb	Hot	0.08	0.07	99
^{209}Bi	Hot	0.15	0.35	97
^{238}U	Hot	0.004	0.001	98

The results in Table 2 shows the suitability of the iCAP RQ ICP-MS for ultratrace multielemental measurement at sub ng·L^{-1} concentration levels in common semiconductor process control matrices.

Improved cold plasma performance

With some earlier RF generator designs, cold plasma wasn't suitable for the routine analysis of high acid concentration samples and further dilution was required, risking contamination from additional sample handling. With the dynamic frequency RF generator on the iCAP RQ ICP-MS, matrix stability in cold plasma is significantly improved allowing for higher acid concentrations to be routinely analyzed.

In order to test this improved cold plasma performance, calibrations at 1, 2, 3, 4 and 5 ng·L^{-1} were achieved for twelve common cold plasma elements in a 7% HNO_3 matrix using the iCAP RQ ICP-MS. A 1 ng·L^{-1} spike recovery test was also performed. The results from these tests are shown in Table 3 and example calibration lines for the cold plasma analysis of ^{7}Li, ^{23}Na, ^{40}Ca and ^{56}Fe are shown in Figures 1 to 4.

Table 3. Cold plasma detection limit (LoD) and background equivalent concentration (BEC) data for 7% HNO_3 using the iCAP RQ ICP-MS. Please note that BEC and LoD values are dependent on the sample measured and were obtained in a non-cleanroom environment. Recovery values are shown as the percentage recovery for a 1 ng·L^{-1} spike in 7% HNO_3.

	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{7}Li	0.02	0.09	98
^{23}Na	0.03	0.52	106
^{24}Mg	0.04	0.07	103
^{27}Al	0.10	0.09	106
^{39}K	0.18	4.78	94
^{40}Ca	0.47	1.45	108
^{52}Cr	0.11	0.69	94
^{55}Mn	0.20	0.81	92
^{56}Fe	0.09	0.76	101
^{58}Ni	0.08	0.14	94
^{59}Co	0.21	0.81	97
^{63}Cu	0.08	0.18	92

As can be seen in Table 3 and Figures 1 to 4, cold plasma on the iCAP RQ ICP-MS effectively suppresses argon based interferences and provides the high sensitivity required for pg·L^{-1} level LoD and BEC values required in semiconductor applications. Spike recoveries from 92% to 108% for twelve elements at 1 ng·L^{-1} in 7% HNO_3 further support the excellent performance of the iCAP RQ ICP-MS in this application.

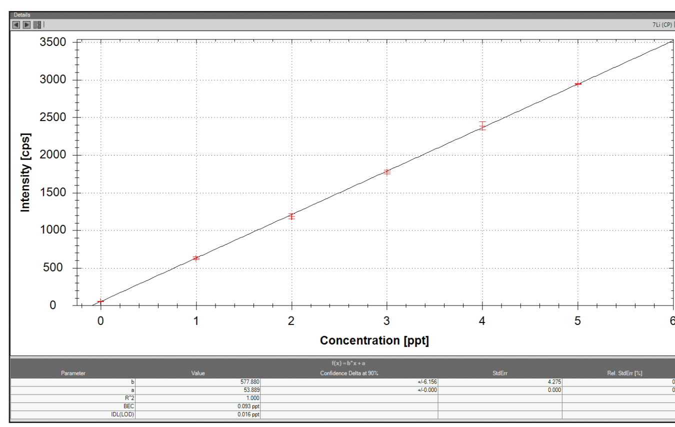

Figure 1. Calibration curve (1 – 5 ng·L^{-1}) for ^{7}Li in cold plasma.

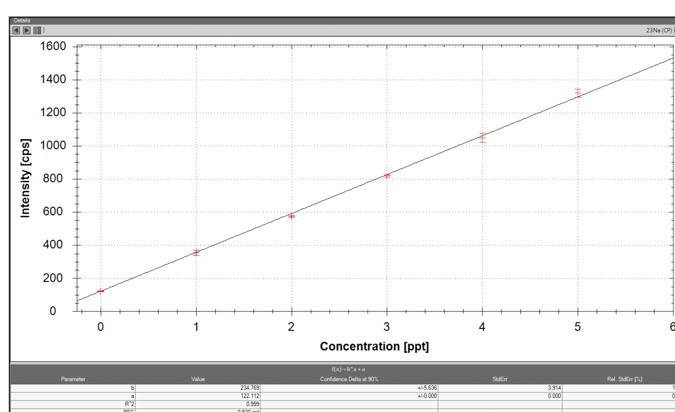

Figure 2. Calibration curve (1 – 5 ng·L^{-1}) for ^{23}Na in cold plasma.

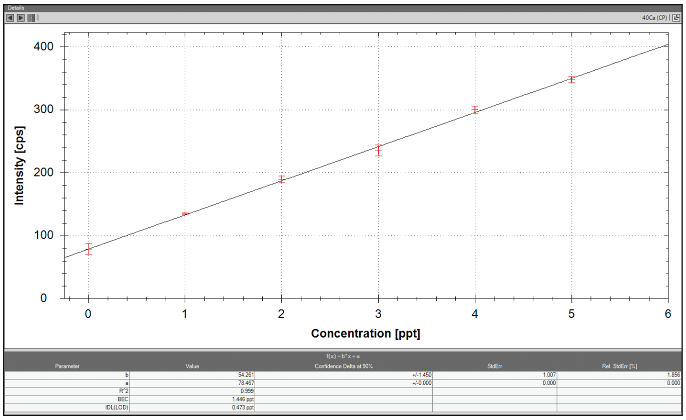

Figure 3. Calibration curve (1 – 5 ng·L^{-1}) for ^{40}Ca in cold plasma.

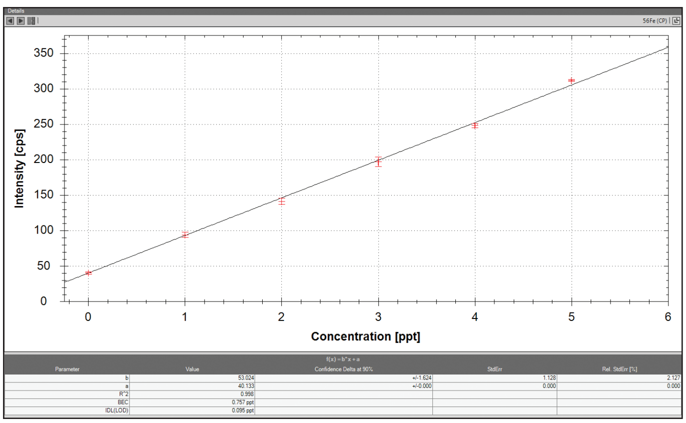

Figure 4. Calibration curve (1 – 5 ng·L^{-1}) for ^{56}Fe in cold plasma.

Conclusion

The Thermo Scientific iCAP RQ ICP-MS has been shown to provide the high sensitivity and freedom from interferences required for the measurement of ultratrace (sub ng·L^{-1}) concentration levels in semiconductor grade acid samples. Fast, automated, in measurement switching between hot and cold plasma is made possible with the dynamic frequency RF generator leading to improved reliability in mixed mode applications.

Products and Reagents used in this Application Note	
100 µL·min^{-1} PFA Nebulizer	1600342
Cold Extraction Lens Kit	1341380
Platinum Tipped Sample Cone	1324530
Platinum Tipped Skimmer Cone	1341430
Fisher Scientific Optima Nitric Acid	A467-500

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